U.S. Miner. Bur. of

Technical Paper 89

DEPARTMENT OF THE INTERIOR
FRANKLIN K. LANE, SECRETARY
BUREAU OF MINES
VAN. H. MANNING, DIRECTOR

COAL-TAR PRODUCTS

AND THE POSSIBILITY OF INCREASING THEIR MANUFACTURE IN THE UNITED STATES

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no. 89
ENGINEERING

BY

HORACE C. PORTER

WITH A CHAPTER ON

COAL-TAR PRODUCTS USED IN EXPLOSIVES

ENGIN STORAGE

BY

C. G. STORM

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Second edition. June, 1916.
First edition issued in February, 1915.

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COAL-TAR PRODUCTS, AND THE POSSIBILITY OF INCREASING THEIR MANUFACTURE IN THE UNITED STATES.

By Horace C. Porter.

INTRODUCTION.[a]

Popular interest in coal tar is centered mainly in dyestuffs and the other refined drugs and chemicals derived from it. The United States for commercial reasons has developed little manufacture of these products, and has been dependent upon European nations for the bulk of her supply.

In considering why this condition exists there must be borne in mind the fact that only a small part of coal tar (about 10 per cent) can be made into drugs and dyes. The other 90 per cent, suited only for the manufacture of pitches and various heavy oils, forms the basis of an industry already well developed in the United States. Increased development of an industry based on only 10 per cent of the tar or on 0.5 per cent of the original coal must depend, in important measure, upon advantageous commercial disposal of the other 90 per cent of the tar or the other 99.5 per cent of the coal.

Coal tar, however, is not the only source of what are commonly known as "coal-tar" dyes and drugs. So-called "gas benzol," or light oil, which is abstracted from coal gas, and is therefore, like tar, a by-product of the carbonization of coal, constitutes an important commercial source of these refined products. High-grade gas coal yields nearly 1 per cent of "gas benzol" by weight, the value of which in the crude state is fully 20 per cent of that of the coal; the light oil of tar, on the other hand, constitutes only 0.1 to 0.2 per cent of the coal. "Gas benzol," unlike tar, has no constituents that can not be utilized in the making of dyes and refined chemical preparations.

About 25 per cent of the combined yield of tar and "benzol" may be made into the dyes, drugs, and refined chemicals for which America has heretofore practically depended on Germany. The gross market value of these refined products made from the 25 per cent portion is probably at least twice that of the pitch and heavy oils recoverable from the 75 per cent portion. On the basis, therefore, of comparative values of products, the manufacture of refined "coal-tar chemicals" appears to be an exceedingly important offshoot of the coke and gas industry.

[a] After this paper was prepared for publication, a committee of the New York section, American Chemical Society, charged with investigating the feasibility of expanding the coal-tar industry in the United States, published a report in the Journal of Industrial and Engineering Chemistry, vol. 6, December, 1914, p. 972. A paper on "The industry of the coal-tar dyes," by B. C. Hesse, appearing on p. 1013 of the same volume of that journal, discusses the commercial and industrial aspects of the present situation. Large shipments of dyestuffs were received at New York in November, 1914, from Germany via Rotterdam, relieving considerably the shortage in those materials.

The United States has the raw material, namely, high-grade coal, in great abundance and of a kind well suited for making all the tar products consumed in the country. Commercial and economic conditions pertaining to the industry have prevented development of the manufacture of dyes and other refined products, but have fostered a well-developed industry in the manufacture of heavy tar oils and various pitches.

In the calendar year 1913 the United States produced about 150,000,000 gallons of coal tar and 7,500,000 gallons of "gas benzol," less than 500,000 gallons of tar being imported. The output of bituminous coal, the source of coal tar, was somewhat more than 475,000,000 tons.[a] Germany, with a coal output of only 295,000,000 tons in the same year, produced more than 250,000,000 gallons of coal tar and about 50,000,000 gallons of benzol, 3,500,000 gallons of tar being imported.

Evidently, in the utilization of coal to make tar and "benzol," the United States is far behind Germany. Also, in the utilization of tar and "benzol" to make the most refined and valuable products, the United States lags behind. Germany exported in the fiscal year ending June 30, 1913, coal-tar dyestuffs worth over $55,000,000, whereas the United States in the same year imported dyestuffs worth $10,000,000, practically the entire consumption.

In the present emergency—the interruption of trade by the European war—imports of coal-tar products to the United States are largely reduced. American business men and consumers are asking: Have we enough of the raw materials to make these products? Can we manufacture and sell them without loss?

The Bureau of Mines, in its investigations looking to the increase of efficiency and the prevention of waste in the use of the Nation's mineral resources, issues this paper in order to point out the present opportunity for developing some industries that hitherto have been comparatively neglected in this country.

RAW MATERIALS AVAILABLE.

Two raw materials are the sources of the so-called "coal-tar products," namely, crude coal tar itself, and light oil or "benzol" stripped from coal gas. It is safe to say that of the total value of coal-tar products used in this country fully one-half is of products which may be made commercially from "benzol." Moreover, the fact that tar contains over 65 per cent of pitch and at least 20 per cent of other constituents not adapted for making dyes and refined preparations, whereas crude "benzol" contains practically no such constituents, greatly enhances the importance of "benzol" as a raw material. These raw materials are obtained as by-products of coke and gas manufacture in by-product ovens and gas retorts.

[a] See Parker, E. W., Production of coal in 1913: Mineral Resources of U. S. for 1913, U. S. Geol. Survey, 1914, p. 711.

The quantity of coal coked in the United States in 1913 was somewhat over 69,000,000 tons,[a] and the quantity used in the manufacture of coal gas in gas retorts was about 4,000,000 tons. With average yields, 7 gallons of tar and 1½ gallons of "benzol" per ton, this amount of coal was capable of yielding as by-products of coking 511,000,000 gallons of tar and 109,500,000 gallons of "benzol." Such amounts of these materials would suffice to produce a very much larger quantity of coal-tar products than was used in this country in 1913. The tar and "benzol" produced from American coal need not be in any way inferior to those produced in Europe.

This country produces, however, less than one-third of the quantity of tar and about 7 per cent of the quantity of "benzol" just named. About 75 per cent (in round numbers 52,000,000 tons) of the coal made into coke in the United States in 1913 was coked in beehive ovens, with total loss of by-products; and of the remaining 25 per cent, 17,000,000 tons, coked in by-product ovens probably less than one-quarter was treated so as to recover "benzol."

SUPPLY OF COAL SUITABLE FOR BY-PRODUCTS MANUFACTURE.

In addition to the coal remaining in the great fields of coking coal in western Pennsylvania, which produce over 60 per cent of the coke made in the United States, this country has an entirely adequate source of tar, "benzol," and other by-products in the coking coals of other districts. Coal fields in West Virginia, Virginia, and eastern Kentucky which now supply many by-product coke ovens and gas works may be drawn on, if necessary, for much more coking coal than they now produce. Most of the western Pennsylvania coals, if coked in by-product ovens, will yield good coke and by-products, so that on the basis of the supply of high-grade coking coal available there seems to be no reason why the use of by-product ovens should not be extended so as to yield whatever tar and "benzol" are required.

In addition to the high-grade coking coals, there are produced in the United States certain other coals the analyses of which indicate possibilities for the production of good yields of tar, "benzol," gas, and ammonia, with medium-grade coke or semicoke as the by-product. In Table 1 are given analyses of a number of coals compiled from Bulletins 22[b] and 85[c] of the Bureau of Mines, certain of the coals being high-grade gas coals now used for making gas, and others being coals that give much promise for gas and coke manufacture with recovery of by-products.

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[a] See Parker, E. W., Manufacture of coke in 1913: Mineral Resources of U. S. for 1913, U. S. Geol. Survey, 1914, p. 471.

[b] Lord, N. W., Analyses of coals in the United States, with descriptions of mine and field samples collected between July 1, 1904, and June 30, 1910, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford. 1913. 1,200 pp.

[c] Fieldner, A. C., Fay, A. H., Smith, H. I., and Sanford, Samuel, Analyses of mine and car samples of coal collected in the fiscal years 1910 to 1913. 1914. 440 pp.

TABLE 1.—*Chemical analyses ("as received" basis) of coking and gas coals from various coal fields.*

[Compiled by A. C. Fieldner.]

Origin of sample.					Air-dry loss of coarse sample.	Moisture at 105° C.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Calorific value, B. t. u.	Phosphorus in coke.
State.	County.	Nearest town.	Bed.	Kind of sample.												
Alabama	Jefferson	Johns	Blue Creek	Mine sample	2.8	3.4	25.8	61.1	9.7	0.9	.....	.....	.....	.....	13,650	0.056
Do	do	Littleton	Mary Lee	do	1.4	2.5	26.9	59.5	11.1	.8	4.8	74.4	1.6	7.3	13,290	.038
Do	do	Mulga	Pratt	do	1.5	2.4	25.9	66.8	4.9	1.5	5.2	81.7	1.5	5.2	14,490	.032
Do.[b]	Tuscaloosa	Searles	Brookwood	do	1.3	2.4	32.4	58.1	7.1	1.4	.....	.....	.....	.....	.....	.030
Colorado[a]	Las Animas	Delagua	"Delagua"	do	2.1	3.3	34.3	52.1	10.3	.6	5.1	71.6	1.4	11.0	12,710	.183
Do.[b]	Gunnison	Crested Butte	.....	do	1.4	3.0	33.6	56.2	7.2	.4	5.4	74.5	1.5	11.0	13,430	.022
Illinois[c]	Franklin	Sesser	No. 6 (Herrin)	Car sample, r. o. m.	3.4	8.1	34.5	48.8	8.6	1.1	5.3	66.1	1.3	17.6	12,060	.018
Do.[c]	Saline	Harrisburg	No. 5 (Springfield	do	5.8	7.8	33.5	50.3	8.4	2.4	5.3	67.4	1.4	15.1	12,420	.021
Kentucky[a]	Letcher	Jenkins	Upper Elkhorn	Mine sample	1.7	3.6	35.8	58.0	2.6	.5	5.4	80.1	1.5	9.9	14,240	.006
Do.[a]	Pike	Hellier	do	do	.5	1.9	35.5	59.9	2.7	.6	5.4	81.4	1.4	8.5	14,690	.006
New Mexico[a]	Colfax	Dawson	Raton	do	1.7	3.3	35.7	48.7	12.3	.7	5.3	70.4	1.2	10.1	12,760	.005
Oklahoma[b]	Pittsburg	Hartshorne	Lower Hartshorne	do	1.8	3.5	36.3	55.3	4.9	1.5	5.7	76.5	1.9	9.5	13,890	.....
Pennsylvania[a]	Allegheny	Scott Haven	Pittsburgh	do	1.4	2.6	32.7	59.4	5.3	.8	5.4	78.2	1.5	8.8	14,090	.....
Do.[a]	Westmoreland	Herminie	do	Car sample, r. o. m.	2.4	3.4	31.8	56.4	8.4	1.1	5.1	74.4	1.4	9.6	13,700	.015
Do.[a]	Washington	Ellsworth	do	Car sample, over ¾-inch.	1.0	2.5	34.5	56.9	6.1	.9	5.3	78.0	1.5	8.2	14,010	.012
Do	Fayette	Connellsville	do	Car sample, r. o. m.	4.2	5.1	27.9	58.3	8.7	.9	4.9	73.1	1.5	10.9	13,370	.010
Do	Indiana	Clymer	Upper Freeport	Mine sample	2.7	3.6	23.6	67.3	5.5	1.3	5.0	79.8	1.3	7.1	14,200	.....
Do	Cambria	Vintondale	Lower Kittanning	do	3.1	3.6	18.6	71.3	6.5	2.0	4.9	80.6	1.2	4.8	14,120	.010
Tennessee	Grundy	Coalmont	Sewanee	Car sample, washed slack.	3.3	4.7	28.8	57.2	9.3	.7	5.0	73.9	1.2	9.9	13,160	.097
Do.[b]	Campbell	Lafolette	Rex	Mine sample	1.5	2.9	32.0	58.3	6.8	1.1	5.2	75.0	1.6	10.3	13,510	.010
Do	Morgan	Petros	Brushy Mountain	Car sample, r. o. m.	4.3	5.6	33.6	51.0	9.8	3.2	5.2	70.1	1.6	10.1	12,840	.....
Do	Rhea	Dayton	Richland	Mine sample	5.9	2.0	28.8	57.4	11.8	1.8	4.9	74.4	1.3	5.8	13,220	.....
Utah[b]	Carbon	Sunnyside	.....	do	1.5	5.1	38.5	48.6	7.8	.5	5.5	70.7	1.6	13.9	12,620	.045
Do.[b]	do	Castlegate	Castlegate	do	3.5	6.1	40.1	45.4	8.4	.6	.....	.....	.....	.....	12,220	.....
Virginia[b]	Russell	Dante	Upper Banner	do	1.8	2.8	35.0	56.4	5.8	.6	5.3	80.1	1.4	6.8	14,150	.030
Do.[b]	Wise	Stonega	Imboden	do	.8	2.2	33.1	58.2	6.5	.7	5.3	77.9	1.5	8.1	13,990	.010
Washington	King	Snowqualmie	.....	do	7.3	8.2	27.2	53.9	10.7	.5	5.2	69.6	1.8	12.2	12,440	.....
Do	Kittitas	Roslyn	Roslyn	Car sample, r. o. m.	5.8	7.8	33.1	44.9	14.2	.5	5.5	64.7	1.4	13.7	11,900	.115
Do	Pierce	Carbonado	"No. 3"	do	3.3	4.7	29.1	50.2	16.0	.5	5.0	67.2	2.1	9.2	12,130	.050
West Virginia[a]	Marion	Monongah	Pittsburgh	Mine sample	1.5	3.0	35.0	56.4	5.6	.7	5.3	77.9	1.4	9.1	13,860	.....
Do	Tucker	Thomas	Lower Kittanning	do	.....	2.2	24.3	65.5	8.0	1.1	.....	.....	.....	.....	14,010	.023
Do	Preston	Bretz	Upper Freeport	Car sample, r. o. m.	.5	1.5	28.6	61.5	8.4	.9	4.9	77.8	1.5	6.5	14,070	.015
Do	Fayette	Kay Moor	Sewell	Mine sample	2.2	3.2	25.1	68.8	2.9	.5	5.1	82.6	1.6	7.3	14,580	.007
Do	Raleigh	Raleigh	Beckley	do	3.8	4.4	18.1	74.0	3.5	.7	5.0	82.7	1.5	6.6	14,470	.....
Do	McDowell	Algoma	Pocahontas No. 3	do	1.9	2.6	18.1	74.6	4.7	.5	4.5	84.3	1.2	4.8	14,560	.005
Do.[a]	Mingo	Glen Alum	War Eagle	Car sample, r. o. m.	1.6	2.9	33.2	58.1	5.8	.7	5.0	78.4	1.4	8.7	14,110	.004
Do.[a]	Logan	Holden	Island Creek or No. 2 Gas.	Mine sample	1.6	1.6	33.7	57.9	6.8	1.3	5.1	76.7	1.3	8.8	13,920	.009

[a] High-grade gas coal. [b] Analysis indicates probability of high yield of gas and by-products.
[c] Coal not used for commercial manufacture of coke, but has yielded fairly good coke in experimental beehive ovens.

As it is plain that there is not likely to be any shortage of suitable coals in this country, the growth of the by-product industry will be controlled by commercial considerations. The greater simplicity and cheapness of the beehive oven, for equal output of coke, makes necessary a less outlay of capital than for a by-product-oven plant; coal-mine or blast-furnace operators using beehive ovens are saved the bother of handling and marketing by-products of coke making; and, whether reasonable or not, an opinion is commonly held that for high-grade metallurgical coke most of the high-volatile coals require mixing with a certain percentage of low-volatile coal in the by-product oven, thus necessitating the use of two grades of coal and the shipment of one or both for a considerable distance to the coking plant. Notwithstanding these factors, the number of by-product ovens has steadily increased in this country in recent years, and the proportion of by-product coke produced rose from 17.1 per cent in 1910 to 27.5 per cent in 1913.

The gross value of the by-products (estimating dyestuffs, etc., in the form of crude intermediate products) wasted by beehive coking in this country in 1913 was over $75,000,000.

The economic production of tar and benzol in the by-product coking process is impossible without advantageous disposal of the coke, gas, and ammonia also obtained. This fact, together with those stated above, will prevent any sudden rapid increase of by-product coking in this country as an outgrowth of an emergency such as the present. In order to supply any immediate, largely increased demand for coal-tar products, the raw materials must be obtained through an increased recovery of benzol, and possibly tar, at existing coke plants, in the establishment of new coal distillation processes, or in the recovery from the tar of certain valuable fractions not now utilized to the best advantage.

PRODUCTION AND DISPOSAL OF COAL TAR.

Of the total coal-tar production of the United States in 1913 (150,000,000 to 155,000,000 gallons), about 75 per cent (115,145,000 gallons) was made in by-product coke ovens. The balance was obtained as a by-product in the manufacture of coal gas in gas retorts.

The increase in the total production in one year, 1912 to 1913, was about 13 per cent, and the aggregate increase during the four preceding years, 1908 to 1912, had been 33 per cent. Evidently there is a growing demand for coal tar and its products aside from that occasioned by the present interruption of trade by the war.

There are other small sources of coal tar, such as gas producers in which bituminous coal is used. These sources, however, are not likely soon to become a large factor in the supply.

Oil and water-gas tars formed from the petroleum used in the manufacture of gas were produced in the United States in 1912 to the amount of 33,930,000 gallons. These tars are thinner than ordinary coal tar but contain many of the same constituents, such as benzene, toluene, xylene, naphthalene, and anthracene, in smaller proportions, and may contribute a little to the raw material of some of the refined products described below, as the demand for raw materials increases.

Coal tar is separated by distillation into a number of fractions, each of which serves as the base for the manufacture of certain refined chemical products. Table 2 shows the proximate composition of average coal tar, including gas-retort tar (not from vertical retorts), and coke-oven tars from various types of ovens. The different tars vary widely in composition because of different operating conditions in the ovens or retorts, and many individual samples differ widely from the average given.

TABLE 2.—*Fractions of average coal tar and their uses.*

First crude separation by distillation.	Light oil	Middle oil (or dead oil).	Heavy oil (including anthracene oil).	Pitch.
Temperatures of distillation.	70°–160° C.	160°–230° C.	230°–360° C.	Above 360° C.
Percentage in tar	3	8	24	65.
Intermediate products, by distillation or expression.	Benzene, toluene, xylene, etc.; phenol.	Phenol, cresols, etc.; naphthalene, heavy hydrocarbons.	Cresols, naphthalene, anthracene; heavy hydrocarbons; quinoline bases.	Soft pitch, hard pitch.
Crude commercial products and their uses.	"Benzol" and solvent naphtha for solvents, paint thinners, motor fuel, gas enrichment.	Creosote oil.	Lamp black.	Pitch, briqueting, protective paints.
		Disinfectants	Road oils, impregnation of timber.	
			Roofing tars.	
			Paving tars.	
Intermediate chemical products.	Nitrobenzene, aniline salts, aniline oil, carbolic acid.	Carbolic acid, picric acid, phthalic acid, naphthols, naphthylamines, salicylic acid.	Anthraquinone, alizarin.	
Refined chemical products, dyes, etc., and their uses.	Nitrotoluenes, diphenylamine and other ingredients of explosives; aniline dyes; hydroquinone and other photographic developers; drugs and medicines.	Picric acid, picrates, and other nitro-compounds for explosives; naphthol dyes and colors, artificial indigo, refined carbolic acid.	Alizarin dyes.	

Whenever commercial conditions favor the manufacture in this country of refined tar products, certain of the crude separations now practiced may be modified so as to render available more of the intermediate substances desired for this manufacture. For example, the creosoting oils as manufactured contain higher phenols, naphthalene, and anthracene, which might be extracted for other purposes if there were a demand.

In considering new sources of supply of coal tar, regard must be had to certain new processes of coal distillation, notably low-temperature or moderate-temperature carbonization. By distilling at 600 to 800° C. coals that coke moderately well, such as are to be had in abundance in the middle west, the southwest, and in the Rocky Mountain fields, excellent yields of tar may be obtained with fair yields of ammonia and fuel gas. The semicoked solid residue has promise of profitable use as a locomotive or domestic smokeless fuel in competition with anthracite coal.

PRODUCTION AND DISPOSAL OF "BENZOL."

Light oil or "benzol," stripped directly from coal gas, is produced in this country in moderate amount. Exact statistics of output are not available, but an estimate based on certain reliable data places the production not utilized in gas enrichment by the producing company itself as under 4,500,000 gallons during the year 1913.

As stated in a previous paragraph, the possible production of "benzol," if the recovery process were applied to all the coal made into coke and gas in this country, would be over 100,000,000 gallons. New "benzol"-recovery plants now being constructed in connection with by-product coke ovens will add probably 2,000,000 gallons to the annual production.

That in the immediate future all the coal gas or coke-oven gas manufactured will be made to give up its "benzol" for purposes of chemical manufactures, is hardly to be expected. Benzene and its homologues are illuminating constituents of gas, and in many cities the maintenance of a minimum illuminating power for gas is required by State law. Therefore, at retort gas-making plants that furnish gas for municipal purposes, the extraction of "benzol" from the gas is not likely to be introduced until the standard of illuminating power gives way to that of heating value. Such a practice would be entirely possible, however, if the demand for "benzol" should justify it, since illuminants derived from petroleum or other oils could be used to replace the "benzol." Owing to the steadily decreasing use of flat-flame jets and the increasing use of mantles, the requirement of a minimum illuminating power for gas has been already discarded in some States and will undoubtedly soon pass out of general use.

Not over 20 per cent of the total gas made in by-product coke ovens in 1913 (about 150,000,000,000 cubic feet) was devoted to public lighting supplies, so that the remaining 80 per cent could have been stripped of its "benzol" had a sufficient demand existed. It is to be noted that the entire make of gas at a coke-oven plant may profitably be stripped of its "benzol," although 50 to 60 per

cent of the gas may be returned for burning in the oven-heating flues. On the basis of the present tonnage of coal made into by-product coke the practicable total production of "benzol" from this source, at 1½ gallons per ton of coal, should accordingly be about 20,000,000 gallons yearly. This production would adequately supply the basic raw material for the aniline dyes and many of the refined "coal-tar products" consumed in this country. The content of pure benzene in the crude light oil stripped from gas is between 65 and 75 per cent.

The coke-oven operators have indicated their willingness to increase their production of "benzol" as the increasing demand from chemical manufacturers or other consumers justifies additional investment in plant.

THE COAL-TAR PRODUCTS.

CREOSOTE OIL.

Between 90,000,000 and 100,000,000 gallons of creosote oil, valued at nearly $6,000,000, were consumed in the United States in the year 1913 for the impregnation and preservation of wood. Probably half of this consumption was for the treatment of railroad ties, and most of the remainder for paving blocks, piling, and structural timber. Two-thirds of the entire consumption was imported.

Coal tar yields 15 to 30 per cent of creosote oil, according to the kind of tar, grade of oil, and the softness desired in the residual pitch. The light oil stripped from gas does not yield creosote. Water-gas tar also yields no creosote, in the strict sense of that term, although the tar is used for creosoting.

The main supply of creosote oil must be sought in coke-oven tar, and the present production of this can not meet more than one-third of the demand. Gas-retort tar may supply 6 or 8 per cent more.

Certain heavier fractions of tar, notably anthracene oil, after chemical treatment are successfully used both in this country and abroad for preserving wood, but their use will not relieve to any large degree the urgent demand for creosote.

American coals and American tars can and do yield creosoting oils of satisfactory quality. The present serious shortage in the supply can be met only by increase of by-product coking operations and by immediate establishment of new coal-distillation processes especially adapted to the recovery of by-products.

LIGHT OILS, "BENZOLS," AND SOLVENT NAPHTHAS.

The light oil distilled from tar contains benzene, toluene, xylene, and small proportions of other compounds. Probably 3,000,000 to 5,000,000 gallons of light oil were obtained from tar in the United States in 1913, and used for solvents, cleansers, pitch-paint thinners,

gas enrichment, and other purposes. This distillate of tar is the source of aniline dyes, certain nitrocompounds used in explosives, and various photographic chemicals, medicines, and drugs, which are largely used but not manufactured in the United States.

HEAVY TARS AND PITCH PRODUCTS.

The heavy tars and pitches obtained as the residuum from distillation of the oils constitute 50 to 80 per cent of the original coal tar, and their profitable disposal is consequently of large commercial importance. The heavy tars and oils, and the soft pitches find application as road binders and road-treating oils, in roofing papers, roofing pitches, and protective and waterproofing paints. Hard pitch, which remains after distillation of the anthracene-oil fraction, is used chiefly for briquetting finely divided fuels. This use of pitch has not been largely developed in the United States and about 100,000 barrels of pitch were exported during the year 1913. New uses for hard pitch, particularly in the electrical industries, are being developed in this country.

The naphthalene and anthracene required for making certain dyestuffs could be extracted from these heavy fractions without detriment to their use for the other purposes named above.

DYESTUFFS.

A detailed discussion of coal-tar dyes is not within the scope of this paper, but a brief outline of their classification and derivation is presented.[a]

ANILINE DYES.

Aniline dyes are made chiefly from benzene, toluene, and phenol, through the preparation of nitrosubstitution products of these and various complicated chemical transformations and combinations with other materials. "Aniline oil," the crude intermediate product made by reduction of nitrobenzene, was imported into the United States in 1913 to the amount of 2,000,000 pounds, and aniline salts, also an intermediate product, to the amount of nearly 5,000,000 pounds. The aniline dyes manufactured in this country are made almost entirely from imported intermediate products. Since 1911, however, aniline itself has been manufactured on a very small scale at one or two plants in the United States.

The quantity of aniline dyes consumed in this country annually would probably not require over 3,000,000 gallons of "benzol," although such an estimate is exceedingly uncertain in the absence of definite information as to the relative quantities of the different dyes

[a] For a comprehensive treatment of this subject from an industrial standpoint, see "The industry of the coal-tar dyes," by B. C. Hesse, Jour. Ind. Eng. Chem., vol. 6, 1914, p. 1013.

used. In making the dyes many other chemicals are used, such as sulphuric, nitric, and acetic acids, caustic alkalies, alcohol, zinc dust, sodium nitrite, chlorine, and bromine, for the supply of which America is not, for the most part, dependent on imports from Europe.

NAPHTHOL DYES.

Naphthalene is the source of a large number of dyes produced through various intermediate products such as the naphthols, naphthylamines, and phthalic acid. The eosin dyes are derived from resorcin, a benzene product, and phthalic acid, a naphthalene product. Artificial indigo, made from naphthalene, was imported into the United States in 1913 to the amount of nearly 8,000,000 pounds, valued at $1,150,000. Naphthalene enough for making the dyes of this class used in America could be obtained from the domestic production of coal tar. Average tar carries between 5 per cent and 10 per cent of naphthalene, which is derived largely from the middle and heavy oil fractions.

ALIZARIN DYES.

Alizarin dyes are made from anthracene by its oxidation to anthraquinone and the conversion of this into various hydroxy-anthraquinones and their derivatives, the alizarins, purpurin, etc. An adequate supply of anthracene for these dyes is at hand in American coal tar. Between 1 per cent and 2 per cent crude anthracene is contained in coal tar, and the amount of pure anthracene in the tar produced in the United States in 1913 was probably at least 8,000,000 pounds. In the same year the imports of alizarin dyes were more than 8,000,000 pounds, valued at $1,825,000.

Other coal-tar dyes, not classifiable under the headings given, are used, but the classes named above cover practically all of the more important dyes.

CARBOLIC ACID.

Pure phenol (or carbolic acid) occurs in the light and middle oils or in the special "carbolic-oil" fraction of coal tar. Between 0.3 and 1.0 per cent of the average crude tar is phenol. It may be manufactured synthetically also from benzene through benzene-sulphonic acid. About 8,300,000 pounds of carbolic acid were imported into the United States in 1913. Probably 8,000,000 pounds was contained in American coal tar, as produced, but only a very small amount was manufactured in America.

Phenol is used not only as a drug and antiseptic, but also to a considerable extent in the manufacture of picric acid for explosives and of certain dyestuffs. Another commercial use of growing importance is the manufacture, by condensing phenol with formaldehyde, of hard, infusible, amorphous substances resembling celluloid.

MISCELLANEOUS CHEMICALS AND DRUGS.

Benzoic and salicylic acids, the photographic developers, monomethylparamidophenol ("metol," "rhodol," or "elon"), hydroquinone, etc., many drugs, such as acetanilide, acetphenetidin (phenacetin), saccharin, antipyrine, acetyl salicylic acid (aspirin), phenolphthalein, and a great variety of other refined chemical products used in comparatively small quantities, are derived from coal tar, chiefly from the light-oil or carbolic-oil fraction. A large part of the amount consumed in the United States has been imported.

COAL-TAR PRODUCTS USED IN MAKING EXPLOSIVES.

By C. G. Storm.

INTRODUCTION.

The coal-tar products of greatest importance as raw materials in the explosives industry of the United States are benzene, toluene, naphthalene, and phenol (carbolic acid). These materials are employed in the manufacture of the various nitrosubstitution products which have gradually found such wide application either as explosives or as ingredients of explosive mixtures.

As explosives the nitrosubstitution products of coal-tar derivatives are used as bursting charges for explosive projectiles, torpedoes, and mines, and also for detonators and primers. As ingredients of explosive mixtures they are used (1) in various low-freezing or nonfreezing mining explosives to lower the freezing point of such mixtures; (2) in certain colloidal or gelatinized explosive mixtures, where their property of forming colloids with the so-called "soluble nitrocellulose" is utilized to produce explosives that are plastic; and (3) in various other types of explosives for the purpose of imparting some desired characteristic. The most commonly known blasting explosives used in this country, black blasting powder and "straight" nitroglycerin dynamite, contain no coal-tar derivatives.

In order to avoid the formation of products having inferior stability, it is generally essential that the benzene, toluene, or other raw material used in the preparation of the nitroderivatives should be of a high degree of purity.

NITROBENZENES.

Mononitrobenzene, commonly known as "oil of mirbane," is little used in the explosives industry because of its volatility, although it is sometimes used as a minor constituent of certain low-freezing dynamites and other types of explosives. It is used much more extensively in soaps, lubricating greases, etc., mainly for the purpose of imparting a more or less agreeable odor. Furthermore, it forms an intermediate product in the preparation of aniline and its many derivatives.

Among the aniline derivatives of importance are tetranitroaniline and tetranitromethylaniline, both of which have in the past few years assumed prominence as detonating explosives for projectiles, mines,

and torpedoes. Many other derivatives of aniline have been found to be applicable as stabilizers or as gelatinizing agents in nitrocellulose smokeless powders. Among such substances are methyl or ethyl phenyl urea, phenyl benzyl ether, phenylacetanilide, formanilide, and diphenylamine. The latter is, however, the only one which has been used in this country.

NITROTOLUENES.

The nitrotoluenes are more extensively used in the explosives industry than any other nitrosubstitution compounds, being employed chiefly for sensitizing certain types of ammonium-nitrate explosives and for lowering the freezing point of the low-freezing dynamites.

In the absence of exact statistics, a rough estimate places the amount of the various grades of nitrotoluenes used in the low-freezing dynamites manufactured in this country in 1913, at about 2,000,000 pounds, while in the "permissible" explosives employed in coal mining probably 250,000 pounds of the same materials were used during the same year.

Pure crystalline trinitrotoluene has proved one of the most efficient explosives for use in explosive shells, torpedoes, and mines, and is extensively used by almost every important military service, including that of this country. In recent years it has also come into use as a substitute for a large proportion of the mercury fulminate in detonators (blasting caps) and as a charge for detonating fuse.

NITRONAPHTHALENES.

The nitronaphthalenes are used to some extent, chiefly as sensitizers in the "short-flame" permissible explosives of the ammonium-nitrate type. Certain derivatives of these compounds, the alkaline salts of nitronaphthalene sulphonic acids, produce, when mixed with sodium nitrate and other ingredients, explosives suitable for coal mining.

PICRIC ACID AND PICRATES.

Picric acid (trinitrophenol) and certain of the picrates are highly important as military shell explosives; the acid is also employed in surgical dressings for burns and wounds.

The manufacture of these compounds depends entirely on phenol (carbolic acid) as a raw material.

The possibilities of the use of the nitroderivatives of coal-tar products in explosives are far greater than is indicated by the above brief summary. Much investigative work on such compounds is being carried on in this country as well as abroad, from which important developments in the explosives art may result. The Bureau of Mines has instituted a systematic research into the preparations and properties of these nitrosubstitution compounds with a view to studying their possibilities in the explosives industry.

COMMERCIAL AND ECONOMIC PHASES OF THE COAL-TAR SITUATION.

By Horace C. Porter.

The raw material for the coal-tar products consumed in America, omitting creosote oil, may be obtained in this country without great delay or unreasonable outlay of capital. It has been shown in the preceding paragraphs that an increase in the production of "benzol" from coal gas, involving only an extension of the recovery process to the existing by-product coke plants which do not sell illuminating gas, would, in conjunction with the present output of tar from coal gas and water gas plants, furnish the requisite raw materials. To supply the total creosote oil consumed an increased production of coal tar will be necessary, and an increased investment, therefore, in coal-carbonizing plants.

The establishment of chemical industries for the manufacture of dyes and other refined tar products in the United States will, however, depend upon a number of commercial factors. The uncertainty as to the duration of present conditions in Europe, and as to the resumption of ruinous competition at the hands of foreign manufacturers, causes American capital to hesitate in entering this field. Although raw material may be cheaply obtained, the risk of financial loss in the operation of such complex and highly specialized processes is a real barrier to the rapid introduction of dye manufacture in this country, or in any country other than the one where it is now well established, namely, Germany.

The Secretary of the Interior, on September 3, 1914, called together in conference a number of the leading manufacturers of coal tar and chemical and pharmaceutical products, for the purpose of determining what aid the Government could render in bringing about an American production of such coal-tar products as hitherto have been imported.

Two definite suggestions were made at this conference:

First, that a system should be instituted in this country whereby if a foreign patent is not used for manufacture within a reasonable time, it will be open to use by American manufacturers.

Second, that a law should be passed whereby unfair competition through the practice known as "dumping" would be cut off. This practice, which is one of the most serious obstacles in the way of developing American manufacture of dyes and coal-tar drugs, consists of selling foreign products in the American market at an unreasonably low price. Since Germany's total exports of dyestuffs are more than five times the amount sent to the United States, the selling

price of the portion sent to this country can readily be placed below cost as a temporary expedient.

German patents on many medicinal preparations preclude their manufacture in this country. On dyestuffs, however, not many American patents are now in force. About 25 per cent of all the coal-tar dyes used are now patented in the United States, but practically all of those most commonly used, and the basic materials for their manufacture, such as crude aniline and alizarin, are not now patented in this country.[a] The patent laws, therefore, can hardly be said to be retarding seriously at present the development of an American dye industry. Their influence was undoubtedly felt at one time and may be of serious moment in the future, with respect to newly discovered dyes.

At present the undeveloped state of the dye industry in America is rather to be ascribed to the great complexity of the industry, the continual changes in demand, the interdependence of many branches of the industry, and the uncertainty of establishing one or more of these on a profitable basis without the support of the entire interlacing fabric, the complete interchange of materials and by-products, and the consequent lowering of costs. For this reason an American industry in these products must be expected to start slowly and in the beginning to bring small returns to the investors.

There seems to be much less uncertainty, however, as to the possibilities for some other manufactures, such as that of carbolic acid, picric acid, and other nitro compounds, photographic developers, and some of the simpler drugs. Furthermore, the fact that for several years aniline dyes in considerable quantity have been manufactured in this country from imported aniline oil and crude intermediates indicates that the complete manufacture here of certain kinds of dyes is not an entirely hopeless undertaking. The preparation of crude aniline from benzene should not offer insurmountable difficulties, either technical or commercial; in fact, this product has been manufactured in a small way in this country for the last three years.

Any apparent shortage of coal tar at the present time, or any lack of an "open market" for obtaining it, is not likely to continue. The disposal of the available supply will adjust itself to the demand. The coal tar produced in the United States for a number of years has been consumed largely by one firm of manufacturers of tar products, but this fact in no way prevents producers of tar from selecting the most advantageous market for their product. Neither is there reason to believe that the present manufacturers of tar products and of benzol will fail to direct the raw materials toward more refined products, such as dyestuffs and drugs, when commercial conditions justify and demand the manufacture of these products.

[a] This statement is based on a communication from Dr. B. C. Hesse, of New York.

PUBLICATIONS ON THE TECHNOLOGY OF COAL.

A limited supply of the following publications of the Bureau of Mines is temporarily available for free distribution. Requests for all publications can not be granted, and applicants should limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines, Washington, D. C.

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl., 9 figs.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl., 7 figs.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls., 7 figs.

BULLETIN 5. Washing and coking tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909, by A. W. Belden, G. R. Delamater, J. W. Groves, and K. M. Way. 1910. 62 pp., 1 fig.

BULLETIN 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker, compiled and revised by H. M. Wilson. 1911. 77 pp., 4 pls., 12 figs.

BULLETIN 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 58 pp., 1 pl., 16 figs.

BULLETIN 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp., 6 figs.

BULLETIN 18. The transmission of heat into steam boilers, by Henry Kreisinger and W. T. Ray. 1912. 180 pp., 78 figs.

BULLETIN 23. Steaming tests of coals and related investigations, September 1, 1904, to December 31, 1908, by L. P. Breckenridge, Henry Kreisinger, and W. T. Ray. 1912. 380 pp., 2 pls., 94 figs.

BULLETIN 24. Binders for coal briquets, by J. E. Mills. 56 pp., 1 fig. Reprint of United States Geological Survey Bulletin 343.

BULLETIN 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 44 pp., 3 pls., 2 figs. Reprint of United States Geological Survey Bulletin 366.

BULLETIN 28. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 51 pp. Reprint of United States Geological Survey Bulletin 323.

BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. Reprint of United States Geological Survey Bulletin 382.

BULLETIN 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp., 8 figs. Reprint of United States Geological Survey Bulletin 393.

BULLETIN 33. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by W. T. Ray and Henry Kreisinger. 50 pp., 10 figs. Reprint of United States Geological Survey Bulletin 403.

BULLETIN 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 33 pp., 9 figs. Reprint of United States Geological Survey Bulletin 412.

BULLETIN 35. The utilization of fuel in locomotive practice, by W. F. M. Goss. 29 pp., 8 figs. Reprint of United States Geological Survey Bulletin 402.

BULLETIN 39. The smoke problem at boiler plants, a preliminary report, by D. T. Randall. 31 pp. Reprint of United States Geological Survey Bulletin 334, revised by S. B. Flagg.

BULLETIN 40. The smokeless combustion of coal in boiler furnaces, with a chapter on central heating plants, by D. T. Randall and H. W. Weeks. 188 pp., 40 figs. Reprint of United States Geological Survey Bulletin 373, revised by Henry Kreisinger.

BULLETIN 49. City smoke ordinances and smoke abatement, by S. B. Flagg. 1912. 55 pp.

BULLETIN 55. The commercial trend of the producer-gas power plant in the United States, by R. H. Fernald. 1913. 93 pp., 1 pl., 4 figs.

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